3D-PRINTED STRUCTURED ADSORBENTS FOR MOLECULAR SEPARATION

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Most adsorbents are produced as porous, micron-sized powder materials and are thus not suitable to be directly used in adsorption processes. In order to avoid excessive pressure drop during flow of gas or liquid streams through a packed bed of adsorbent, these powders are shaped into larger particles or structured adsorbents. Extrudates, beads or pellets with a size of several millimeters are widely used in industrial processes. The most important disadvantages of such particles include the relatively large pressure drop they generate at high flow rates and the presence of mass transfer limitations as a result of slow diffusion of molecules to the core of the particles. A trade-off between these two effects limits the possibilities to optimize packed bed adsorptive separation processes; e.g. decreasing pellet size allows to reduce mass transfer limitations but this in turn leads to larger pressure drops. In practice, bed geometry (length/width of the packed bed) is adapted to limit pressure drop. Nevertheless, classical packed beds are not ideal for processes in which very short cycle times or very high gas or liquid velocities are required.

Other types of adsorbent formulation that allow eliminating the limitations mentioned above are thus of large interest. Monolithic adsorbents are superior to classical packed bed adsorbents in terms of pressure drop and mass transfer kinetics. The honeycomb structure, mostly known from catalytic exhaust treatment in the automotive industry, is a well-known example, but monolithic structures are also used in liquid chromatography and heterogeneous catalysis. Nevertheless, the production of monoliths is complicated; classical extrusion processes only offer a very limited flexibility in the geometric properties of the monolith while polymerization processes are not suited for the production of materials for high temperature applications.

Recently, 3D-printing methods have tremendously expanded the possibilities in material synthesis, with much more degrees of freedom. In the present work, a new method to develop monolithic structures is tested for its use in gas and liquid adsorptive separation. Layers of adsorbent fibers are printed on top of each other, where each layer can have a different orientation. Fiber thickness and interdistance can be varied easily. This allows to generate structured adsorbents with a very high porosity, interconnected channels and high adsorption capacity. Zeolite (13X, ZSM-5, SAPO-34) and MOF (ZIF-8) based monoliths were produced in different geometries by this 3D-printing method. The obtained materials were characterized via Hg and Ar porosimetry to determine micro-, meso- and macroporosity. Adsorption capacities for CO_2, N_2 and CH_4 were obtained via pure component isotherms measurements to allow comparison with the adsorbents in their initial powder form. It was demonstrated that the method developed at VITO allows to obtain materials with very large adsorption capacity and very good accessibility. Subsequently, the monoliths were subjected to breakthrough separation experiments. Two model systems were looked at: the separation of CO_2 from flue gas or biogas and the recovery of biobutanol from the ABE fermentation process. Promising separation properties were obtained, with large selectivities, large capacities and low pressure drop. Depending on the chemical composition of the adsorbents, fast regeneration could be obtained under isothermal and thermal swing conditions.

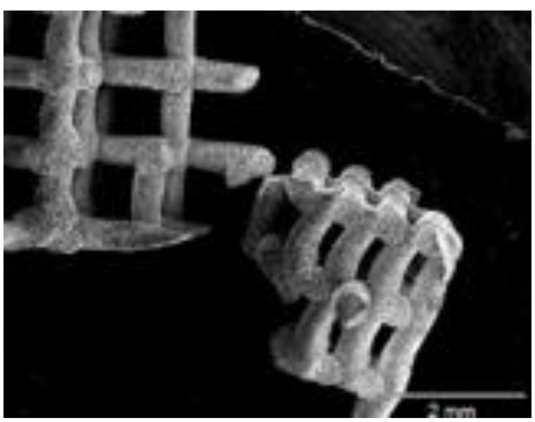

Figure 1 – SEM picture of a monolithic structure. Top view (left), Side view (right)

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